

AMENDMENTS TO THE CLAIMS

This listing of claims will replace all prior versions, and listings, of claims to the application.

Listing of Claims:

1-7 (canceled)

8. (previously amended) A method of making a carboxylated carbohydrate product which comprises: oxidizing a carbohydrate compound by reacting it in an aqueous system with a sufficient amount of a primary oxidant selected from the group consisting of hindered heterocyclic oxammonium salts in which the carbon atoms adjacent the oxammonium nitrogen lack .alpha.-hydrogen substitution, the corresponding amines, hydroxylamines, and nitroxides of these oxammonium salts, and mixtures thereof, in which the nitroxide is 2,2,2',2',6,6,6',6'octa- methyl-4,4'-bipiperidinyl-1,1'-dioxy di-radical, and a secondary oxidant selected from chlorine dioxide and latent sources of chlorine dioxide in a sufficient amount to induce an increase in carboxyl substitution in the carbohydrate of at least 2 meq/100 g.

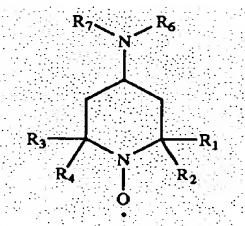
9. (previously amended) A method of making a carboxylated carbohydrate product which comprises: oxidizing a carbohydrate compound by reacting it in an aqueous system with a sufficient amount of a primary oxidant selected from the group consisting of hindered heterocyclic oxammonium salts in which the carbon atoms adjacent the oxammonium nitrogen lack .alpha.-hydrogen substitution, the corresponding amines, hydroxylamines, and nitroxides of these oxammonium salts, and mixtures thereof, in which the nitroxide is 2,2,6,6-tetramethyl-4-hydroxypiperidinyl-1-oxy free radical, and a secondary oxidant selected from chlorine dioxide and latent sources of chlorine dioxide in a sufficient amount to induce an increase in carboxyl substitution in the carbohydrate of at least 2 meq/100 g.

10. (previously amended) A method of making a carboxylated carbohydrate product which comprises: oxidizing a carbohydrate compound by reacting it in an aqueous system with a sufficient amount of a primary oxidant selected from the group consisting of hindered heterocyclic oxammonium salts in which the carbon atoms adjacent the oxammonium nitrogen lack .alpha.-hydrogen substitution, the corresponding amines, hydroxylamines, and nitroxides of these oxammonium salts, and mixtures thereof, in which the nitroxide is 2,2,6,6-tetramethyl-4-methoxypiperidinyl-1-oxy free radical, and a secondary

oxidant selected from chlorine dioxide and latent sources of chlorine dioxide in a sufficient amount to induce an increase in carboxyl substitution in the carbohydrate of at least 2 meq/100 g.

11. (previously amended) A method of making a carboxylated carbohydrate product which comprises: oxidizing a carbohydrate compound by reacting it in an aqueous system with a sufficient amount of a primary oxidant selected from the group consisting of hindered heterocyclic oxammonium salts in which the carbon atoms adjacent the oxammonium nitrogen lack .alpha.-hydrogen substitution, the corresponding amines, hydroxylamines, and nitroxides of these oxammonium salts, and mixtures thereof, in which the nitroxide is 2,2,6,6-tetramethyl-4-benzyloxypiperidinyl-1-oxy free radical, and a secondary oxidant selected from chlorine dioxide and latent sources of chlorine dioxide in a sufficient amount to induce an increase in carboxyl substitution in the carbohydrate of at least 2 meq/100 g.

12. (previously amended) A method of making a carboxylated carbohydrate product which comprises: oxidizing a carbohydrate compound by reacting it in an aqueous system with a sufficient amount of a primary oxidant selected from the group consisting of hindered heterocyclic oxammonium salts in which the carbon atoms adjacent the oxammonium nitrogen lack .alpha.-hydrogen substitution, the corresponding amines, hydroxylamines, and nitroxides of these oxammonium salts, and mixtures thereof, in which the nitroxides are compositions having the structure

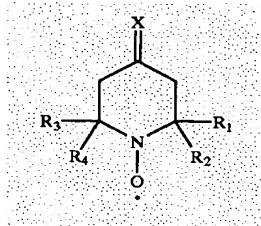


in which R₁- R₄ are one to four carbon alkyl groups but R₁ with R₂ and R₃ with R₄ may together be included in a five or six carbon alicyclic ring structure, and R₆ is hydrogen or C₁-C₅ alkyl, and R₇ is hydrogen, C₁- C₈ alkyl, phenyl, carbamoyl, alkyl carbamoyl, phenyl carbamoyl, or C₁- C₈ acyl, and a secondary oxidant selected from chlorine dioxide and latent sources of chlorine dioxide in a sufficient amount to induce an increase in carboxyl substitution in the carbohydrate of at least 2 meq/100 g.

13. (original) The method of claim 12 in which the nitroxide is 2,2,6,6-tetramethyl-4-aminopiperidinyl-1-oxy free radical.

14. (original) The method of claim 12 in which the nitroxide is 2,2,6,6-tetramethyl-4-acetylaminopiperidinyl-1-oxy free radical.

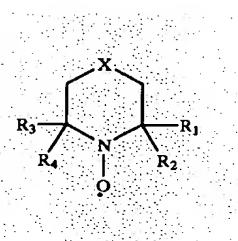
15. (previously amended) A method of making a carboxylated carbohydrate product which comprises: oxidizing a carbohydrate compound by reacting it in an aqueous system with a sufficient amount of a primary oxidant selected from the group consisting of hindered heterocyclic oxammonium salts in which the carbon atoms adjacent the oxammonium nitrogen lack .alpha.-hydrogen substitution, the corresponding amines, hydroxylamines, and nitroxides of these oxammonium salts, and mixtures thereof, in which the nitroxides are compositions having the structure



in which R₁- R₄ are one to four carbon alkyl groups but R₁ with R₂ and R₃ with R₄ may together be included in a five or six carbon alicyclic ring structure, and X is oxygen, sulfur, NH, N-alkyl, NOH, or NOR₈ where R₈ is lower alkyl, and a secondary oxidant selected from chlorine dioxide and latent sources of chlorine dioxide in a sufficient amount to induce an increase in carboxyl substitution in the carbohydrate of at least 2 meq/100 g.

16. (original) The method of claim 15 in which the nitroxide is 2,2,6,6-tetramethyl-4-piperidone-1-oxy free radical.

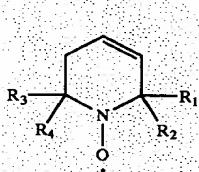
17. (previously amended) A method of making a carboxylated carbohydrate product which comprises: oxidizing a carbohydrate compound by reacting it in an aqueous system with a sufficient amount of a primary oxidant selected from the group consisting of hindered heterocyclic oxammonium salts in which the carbon atoms adjacent the oxammonium nitrogen lack .alpha.-hydrogen substitution, the corresponding amines, hydroxylamines, and nitroxides of these oxammonium salts, and mixtures thereof, in which the nitroxides are compositions having the structure



wherein R₁-R₄ are one to four carbon alkyl groups but R₁ with R₂ and R₃ with R₄ may be linked into a five or six carbon alicyclic ring structure, X is oxygen, sulfur, -alkyl amino, or acyl amino, and a secondary oxidant selected from chlorine dioxide and latent sources of chlorine dioxide in a sufficient amount to induce an increase in carboxyl substitution in the carbohydrate of at least 2 meq/100 g.

18. (original) The method of claim 17 in which the nitroxide is 3,3,5,5-tetramethylmorpholine-1-oxy free radical.

19. (previously amended) A method of making a carboxylated carbohydrate product which comprises: oxidizing a carbohydrate compound by reacting it in an aqueous system with a sufficient amount of a primary oxidant selected from the group consisting of hindered heterocyclic oxammonium salts in which the carbon atoms adjacent the oxammonium nitrogen lack α -hydrogen substitution, the corresponding amines, hydroxylamines, and nitroxides of these oxammonium salts, and mixtures thereof, in which the nitroxides are compositions having the structure

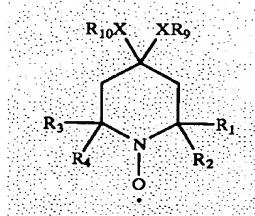


wherein R₁-R₄ are one to four carbon alkyl groups but R₁ with R₂ and R₃ with R₄ may be linked into a five or six carbon alicyclic ring structure, and a secondary oxidant selected from chlorine dioxide and latent sources of chlorine dioxide in a sufficient amount to induce an increase in carboxyl substitution in the carbohydrate of at least 2 meq/100 g.

20. (original) The method of claim 19 in which the nitroxide is 3,4-dehydro-2,2,6,6,-tetramethylpiperidinyl-1-oxy free radical.

21. (previously amended) A method of making a carboxylated carbohydrate product which comprises: oxidizing a carbohydrate compound by reacting it in an aqueous system with a sufficient amount of a primary oxidant selected from the group consisting of

hindered heterocyclic oxammonium salts in which the carbon atoms adjacent the oxammonium nitrogen lack .alpha.-hydrogen substitution, the corresponding amines, hydroxylamines, and nitroxides of these oxammonium salts, and mixtures thereof, in which the nitroxides are compositions having the structure



wherein R₁- R₄ are one to four carbon alkyl groups but R₁ with R₂ and R₃ with R₄ may together be included in a five or six carbon alicyclic ring structure, X is methylene, oxygen, sulfur, or alkylamino, and R₉ and R₁₀ are one to five carbon alkyl groups and may together be included in a five or six member ring structure which, in turn, may have one to four lower alkyl or hydroxy alkyl substituents, and a secondary oxidant selected from chlorine dioxide and latent sources of chlorine dioxide in a sufficient amount to induce an increase in carboxyl substitution in the carbohydrate of at least 2 meq/100 g.

22. (original) The method of claim 21 in which each X is oxygen, the oxygen atoms being linked by a two to three carbon alkyl chain to form a cyclic ketal substituent.

23. (original) The method of claim 22 in which the nitroxide composition is the 1,2-ethanediol cyclic ketal of 2, 2, 6, 6-tetramethyl-4-piperidone-1-oxy free radical.

24. (original) The method of claim 22 in which the nitroxide composition is the 1,3-propanediol cyclic ketal of 2,2,6,6-tetramethyl-4-piperidone-1-oxy free radical.

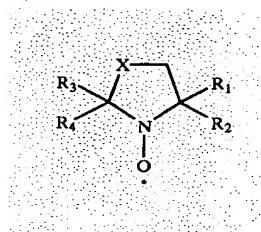
25. (original) The method of claim 22 in which the nitroxide composition is the 2,2-dimethyl-1,3-propanediol cyclic ketal of 2,2,6,6-tetramethyl-4-piperidone-1-oxy free radical.

26. (original) The method of claim 22 in which the nitroxide is the glyceryl cyclic ketal of 2,2,6,6-tetramethyl-4-piperidone-1-oxy free radical.

27. (previously amended) A method of making a carboxylated carbohydrate product which comprises: oxidizing a carbohydrate compound by reacting it in an aqueous system with a sufficient amount of a primary oxidant selected from the group consisting of hindered heterocyclic oxammonium salts in which the carbon atoms adjacent the oxammonium nitrogen lack .alpha.-hydrogen substitution, the corresponding amines, hydroxylamines, and nitroxides of these oxammonium salts, and mixtures thereof, in which

the nitroxides have a five atom ring structure with 2,2,5,5 lower alkyl substitution, and a secondary oxidant selected from chlorine dioxide and latent sources of chlorine dioxide in a sufficient amount to induce an increase in carboxyl substitution in the carbohydrate of at least 2 meq/100 g.

28. (original) The method of claim 27 in which the nitroxides are compositions having the structure

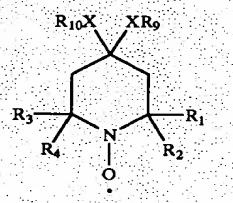


in which R₁-R₄ are one to four carbon alkyl groups but R₁ with R₂ and R₃ with R₄ may together be included in a five or six carbon alicyclic ring structure, and X may be methylene, sulfur, oxygen, --NH, or NR₁₁, in which R₁₁ is a lower alkyl.

29. (original) The method of claim 28 in which the nitroxide composition is 2,2,5,5-tetramethylpyrrolidinyl-1-oxy free radical.

30-63 (canceled)

64. (previously amended) A method of making a carboxylated carbohydrate product which comprises: oxidizing a carbohydrate compound by reacting it in an aqueous system with a sufficient amount of a primary oxidant selected from the group consisting of hindered cyclic nitroxides having the composition



wherein R₁-R₄ are one to four carbon alkyl groups but R₁ with R₂ and R₃ with R₄ may together be included in a five or six carbon alicyclic ring structure, X is methylene, oxygen, sulfur, or alkylamino, and R₉ and R₁₀ are one to five carbon alkyl groups and may together be included in a five or six member ring structure which, in turn, may have one to four lower alkyl or hydroxy alkyl substituents; and a secondary oxidant selected from chlorine dioxide and latent sources of chlorine dioxide in a sufficient amount to induce an increase in carboxyl substitution in the carbohydrate of at least 2 meq/100g.

65. (original) The method of claim 64 in which each X is oxygen, the oxygen atoms being linked by a two to three carbon alkyl chain to form a cyclic ketal substituent.

66. (original) The method of claim 65 in which the cyclic ketal is selected from the group consisting of the 1,2-ethanediol, 1,3-propanediol, 2,2-dimethyl-1,3-propanediol, and glyceryl ketals of 2,2,6,6-tetramethyl-4-piperidone-1-oxy free radicals and mixtures thereof.

67. (original) The method of claim 66 in which the nitroxide composition is the 1,2-ethanediol cyclic ketal of 2,2,6,6-tetramethyl-4-piperidone-1-oxy free radical.

68. (original) The method of claim 66 in which the nitroxide composition is the 1,3-propanediol cyclic ketal of 2,2,6,6-tetramethyl-4-piperidone-1-oxy free radical.

69. (original) The method of claim 66 in which the nitroxide composition is the 2,2-dimethyl-1,3-propanediol cyclic ketal of 2,2,6,6-tetramethyl-4-piperidone-1-oxy free radical.

70. (original) The method of claim 65 in which the nitroxide is the glyceryl cyclic ketal of 2,2,6,6-tetramethyl-4-piperidone-1-oxy free radical.

71. (original) The method of claim 64 in which the carbohydrate is a polymeric compound and which further comprises protecting the carbohydrate against degree of polymerization (D.P.) loss by further treating it in aqueous suspension with a stabilizing agent selected from the group consisting of oxidizing agents and reducing agents in order to remove any substituents which tend to cause molecular chain breakage.

72. (original) The method of claim 71 in which the carbohydrate compound is cellulose.

73. (original) The method of claim 72 which further comprises treating the carboxylated cellulose fibers with a tertiary oxidizing agent to stabilize the product by substantially converting any aldehyde substituents to additional carboxyl groups.

74. (original) The method of claim 73 in which the tertiary oxidant is selected from the group consisting of alkali metal chlorites, a chlorine dioxide/hydrogen peroxide mixture, and peracids.

75. (original) The method of claim 74 in which the tertiary oxidant is a mixture of chlorine dioxide and hydrogen peroxide.

76. (original) The method of claim 74 in which the tertiary oxidant is sodium chlorite.

77. (canceled)

78. (original) The method of claim 72 in which the cellulose is fibrous and is selected from the group consisting of bleached and unbleached kraft wood pulps, prehydrolyzed kraft wood pulps, sulfite wood pulps and mixtures thereof.

79. (original) The method of claim 78 in which the cellulose fiber is recycled secondary fiber.